

# Handbook of Thermoplastic Polyesters


Volume 1

Homopolymers, Copolymers, Blends,  
and Composites

Edited by Stoyko Fakirov

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Cover photo: SAXS pattern from a drawn PET/PE blend taken at DESY-Hamburg (for more details see chapter 23).

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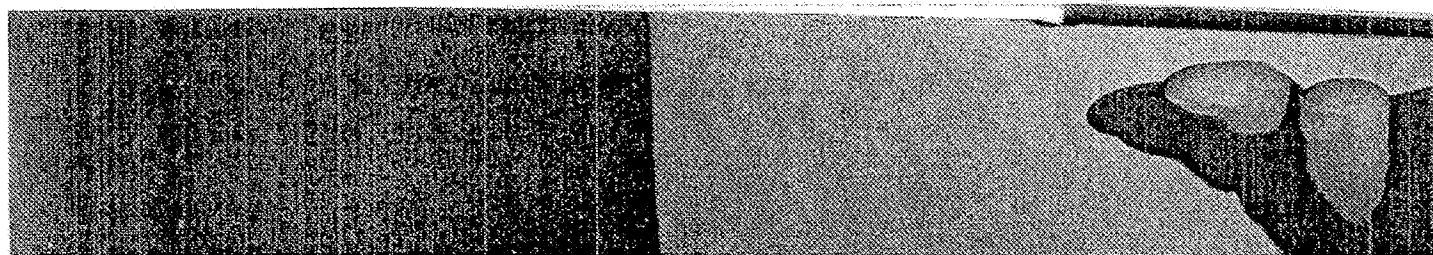
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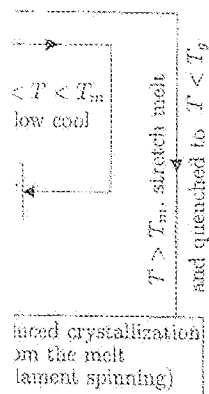
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The polyesters do not have a commercial synthetic application, they enjoy a wide application in synthetic fibers (Trevira, for example). They found new, interesting applications in many other areas. It is not an alternative to the textile industry, but a complement, and, what is more, the textile industry is growing. While PET has rather a wide application in the textile industry (Mylar, Hostafan), PET has a wide application in the packaging industry. PET is a monopoly. Nowadays, the growth of PET is 10%.

All of these opportunities are due to the properties, originating from the importance of its low cost. It is easily obtained in the glass transition region. PET is chemically very stable and very attractive as a packaging material. The presence of functional groups in the polymer chain (additional condensation reactions) leads to high enough (preferably) high molecular weight problems, as well as to solid state postcondensation. Since poly(butylene terephthalate) is in chemical composition much higher crystallinity is relatively limited. PET is relatively limited. PET is relatively limited.





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processing behavior  
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der (Figure 1), such as amorphous (transparent), "oriented mesomorphic" (transparent), spherulitically crystallized (opaque), and oriented crystallized (transparent) from strain-induced crystallization. Transparency, mechanical properties, dyeability, storage stability and gas barrier are properties controlled by the nature of the order in the finished articles made from PET.

Secondly, the rheological properties of PET differ from those of other common thermoplastic polymers; this also controls the way the polymer is processed and the properties of the finished article. Condensation polymers generally have low melt strength because of their low degree of polymerization. There is one noteworthy difference between the method PET filaments and fibers are produced and that used for producing PET sheets, films, or bottles. With filaments and fibers, direct shape forming is possible from the melt, while with films and bottles it is essential to first make an amorphous intermediate (sheet or preform) by quench cooling from the melt. Then the intermediate is softened by heating to a temperature  $\sim 30^\circ\text{C}$  above the  $T_g$ , when it has enough strength to support itself but is pliable enough to be biaxially stretched. Direct biaxial stretching of the melt is possible with polyolefins, but not with standard PET because of its low melt strength. For this reason, conventional film blowing and extrusion blow molding techniques (where biaxial stretching is applied to the melt) are not suitable for this polymer. The PET melt cannot support its own weight long enough for controlled biaxial stretching to take place. In the case of PET filaments, despite the low melt strength, this problem does not arise because the filament is formed by accelerating the melt in the direction of gravity.

## 2. Molecular weight selection

The selection of the appropriate grade of PET for a specific end-use requires considerable care. In this context, one of the first considerations is the molecular weight of the polymer, which is generally reported as intrinsic viscosity (I.V.) or limiting viscosity number,  $[\eta]$ . The relationship between  $[\eta]$  and molecular weight depends on the conditions of measurement [3,4]. Although  $[\eta]$  is primarily related to the molecular weight, its value may also show a significant dependence on the solvent system and temperature used for the measurement. Also, I.V. may be obtained by an extrapolation procedure based on flow measurements made at several concentrations, or by an approximation from a single concentration measurement [5]. Thus,  $[\eta]$  values should strictly be compared only when obtained by means of the same measurement method. Nevertheless, to give an approximate idea, I.V. values of 0.40, 0.63, 0.72, and 1.00 dL/g correspond to number average molecular weights of 10 000, 18 000, 24 000, and 40 000 g/mol, respectively (see also Chapter 16).

Table 1. The intrinsic viscosity range of PET

PET	$[\eta]$ (dL/g)
Fiber grade	
• Textile	0.40–0.70
• Technical	0.72–0.98
Film grade	
• Biaxially oriented film	0.60–0.70
• Sheet grade for thermoforming	0.70–1.00
Bottle grade	
• Water bottles	0.70–0.78
• Carbonated soft drink grade	0.78–0.85

PET fiber grades are homopolyesters made in a wide range of molecular weights to meet different end-use requirements. The I.V. range is usually 0.40 to 0.98 dL/g. Fiber grade PET contains some titanium dioxide to reduce luster and provide whiteness. Speciality chemicals, such as optical brighteners and colored pigments, are sometimes added during polymer production. Small amounts of comonomer may also be added to impart specific properties such as enhanced dyeability, flame retardation, and antistatic properties.

PET film grades are homopolyesters with I.V. in the range 0.55 to 0.65 dL/g and contain slip additives that are added during polymerization. They give rise to a rough surface, preventing film layers from sticking to one another. Color modifiers are sometimes added to the polymer [2]. Sheet grades for thermoforming have I.V. in the range of 0.70–1.00 dL/g.

The requirements for PET bottle grade resins are high I.V. (0.7–0.85 dL/g) and low acetaldehyde (AA) content. Although of no concern in fibers and films, AA is of paramount importance in bottle applications. Most bottle grade PETs today are copolyesters slightly modified through addition of 1–2% isophthalic acid (IPA) or cyclohexanedimethanol during polymerization. These modifiers lower the melting point and decrease the rate of crystallization, effectively broadening the processing window of the resin.

The intrinsic viscosity range of PET for the three major application areas is summarized in Table 1.

### 3. Industrial processes for the production of PET

Melt polymerization is used to produce filaments, fibers, and films (Figure 2). An industrial plant may produce textile grade or film grade chips for conversion by a downstream converter. Alternatively, modern plants may have direct melt spinning or film extrusion setups. That is, the PET melt with the appropriate I.V. and additives from the final reactor of a melt

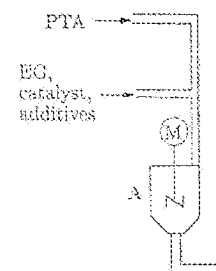


Figure 2. Diagram of a production: A: paste r densation reactor, E f

polymerization line 1

With bottle grade stages: melt and solid from those for other standard for AA in a high I.V. PET resin can give I.V. up to unacceptably high (to be made by a two-produced by melt p about 0.6–0.64 dL/g amorphous resin is 1. The SSP temperature process allows the 1 the melt polymeriza < 1 ppm. The lower AA is minimized (se

In the next section will be described with and additives) for the intermediate chips for in Section 3.2 and a

#### 3.1. Melt polymer films, and int

The raw materials for purified terephthalic